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(54) METHOD AND APPARATUS FOR THE FORMATION OF NITROUS OXIDE

(71) I, TASUKA SUWA, a Japanese subject of, 4—43—4, Saginomiya, Nakano-ku, Tokyo, Japan, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

THIS INVENTION relates to a method and apparatus for forming nitrous oxide by the direct oxidation of ammonia and in particular to the use of a multi-stage catalytic system in such a process, and to the subsequent purification of the produced nitrous oxide.

In the conventional process such as described in Japanese Patent Specification No. 298,838, for the production of nitrous oxide by the catalytic oxidation of ammonia by oxygen, the product gases containing nitrous oxide produced by the catalytic reaction are cooled, replenished with ammonia and oxygen, and then recycled in order to increase the concentration of nitrous oxide. When the conventional process is applied for the production of nitrous oxide on a commercial basis, a blower with large capacity must be used for recycling large volumes of gases amounting to several tens of times that of the product, nitrous oxide. Consequently, the consumption of electricity for operating the blower is comparatively high because it recycles the gases which do not participate in the main reaction.

In accordance with the present invention, there is provided a method of forming nitrous oxide by the catalytic oxidation of ammonia with oxygen, the method comprising causing a mixture of ammonia and oxygen to contact successively a plurality of spaced zones of catalyst arranged in series with the formation of nitrous oxide in each zone, cooling the gaseous mixture formed in each catalyst zone to a temperature not below the dew point of water in the mixture prior to feeding it to the next catalyst zone and causing it to contact the catalyst in the next zone together with newly added ammonia without separating the nitrous oxide, and recovering nitrous oxide from the product gas mixture obtained from the last zone.

Very efficient cooling may be achieved by circulating a heat abstraction medium in the catalyst zone whereby to cool the gaseous mixture formed in that zone by indirect heat exchange.

Thus, further in accordance with the invention, there is provided apparatus comprising a multi-stage reactor having means for supporting at least two catalyst beds in series, the catalyst beds being spaced from one another, means for supplying a reaction mixture of ammonia and oxygen to the first catalyst bed, means for supplying a reaction mixture comprising fresh ammonia and the gaseous product of the previous catalyst bed to each succeeding catalyst bed after the first, and means associated with at least each of the catalyst beds except the last for circulating a heat abstraction medium within the catalyst bed for indirect heat exchange with the gaseous reaction mixture in that bed.

In one suitable embodiment, the catalyst beds may be disposed one above the other in vertically spaced relationship in a tower reactor.

Preferably, at least three catalyst zones are used whereby a high concentration of nitrous oxide may be accumulated in the product gas mixture without any risk of explosion.

The process of the invention is highly efficient and high conversion rates may be achieved, and the percentage of nitrous oxide available in the product gas mixture may be much higher than that from the prior art process.

When the mixture of ammonia and oxygen passes through the catalyst layer, the follow-

ing four oxidation reactions are carried out:

$$2NH_3+2O_2=N_2O+3H_2O+136.8 \text{ Kcal.} \quad (1)$$

$$4NH_3+5O_2=4NO+6H_2O+214.96 \text{ Kcal.} \quad (2)$$

$$4NH_3+7O_2=4NO_2+6H_2O+269.5 \text{ Kcal.} \quad (3)$$

$$4NH_3+3O_2=2N_2+6H_2O+301.36 \text{ Kcal.} \quad (4)$$

If the object is to produce nitrous oxide, it is essential to adopt conditions of reaction which favour reaction (1). Preferred conditions are:

a reaction temperature of at least 300°C, preferably 300 to 340°C;

a space velocity of at least 1,000 and preferably 1000 to 1500;

manganese-bismuth oxide as a catalyst.

As may be noted from equation (1), three mols of water are produced as a by-product to one mole of nitrous oxide. Water in a liquid state is toxic to the catalyst and that is why the gaseous mixture formed in each catalyst zone and cooled before being fed to the next catalyst zone to avoid overheating in that next catalyst zone should not be cooled below the dew point.

The gaseous mixture is also replenished with ammonia, prior to being fed to the next catalyst zone to undergo further oxidation. Nitrogen dioxide, which is a by-product produced as shown in chemical equation (3), may react with the newly added ammonia to produce a small quantity of ammonium nitrate but this reaction is not harmful to the main reaction because the ammonium nitrate decomposes according to equation (5), when it passes through the catalyst layer at a temperature of approximately 260°C.

$$NH_4NO_3=2H_2O+N_2O+13.6 \text{ Kcal.} \quad (5)$$

By adding the ammonia to the gas mixture prior to its passage through each catalyst zone after the first, a product gas mixture may be obtained which contains 30—40 percent of nitrous oxide. Moreover, a substantial decrease in the consumption of electric power compared to the conventional processes can be obtained by this invention when practiced in conjunction with efficient purification and concentration systems such as described hereinafter.

In the description of this invention, some similarities may be found with reports, A. P. Zasorin and V. I. Atroshchenko Zhr. Prikl. Khim, 40 (7) 1414—19 (1967) and Chemical Abstracts, *67* (24) 110146t (1967). These reports, however, relate to the manufacture of nitrogen dioxide as a raw material for the production of nitric acid. A platinum net is used as a catalyst, and the gases are produced at a higher temperature and must be cooled down to a great extent in order to operate at a high space velocity. The authors of these reports offer a set of several independent reactors equipped with cooling systems of high efficiency for the use of a commercial plant. The reduction of construction cost and the simplification of the plant cannot be achieved by such a plant for the production of nitrous oxide.

The preferred embodiment of the present invention involves the manufacture of nitrous oxide using bismuth-manganese oxide catalyst which is highly efficient and only one multi-stage reactor equipped with several catalyst beds, cooled by a built-in cooling system. The heat of reaction can thus be smoothly removed within the catalyst layer, and nitrous oxide can be manufactured at a lower cost.

With respect to the purification, separation and concentration of nitrous oxide from the produced gases, which comprise a mixture of nitrous oxide, oxygen, nitrogen, ammonia and small quantities of higher oxides of nitrogen, this invention also provides a system which is much different from the conventional one. While the conventional method uses one scrubber and two desorption towers with high loss of nitrous oxide, the system proposed for use with the method of the invention comprises two scrubbing towers and two desorption towers, which enables recovery of almost all the product. Moreover, the consumption of electric power can be reduced considerably, because the quantity of recycled gases is far smaller than that of the conventional process.

In the concentration system of the conventional process, the gaseous product gained from the reactor is compressed, and washed with water by the use of a scrubber. Water taken out from the scrubber and containing nitrous oxide is led to the first stage pressure reducing desorption tower to discharge nitrous oxide of 90 percent purity, which is returned to the intake side of the compressor, together with nitrous oxide generated by the reactor and scrubbed, but the off-gases from the top of the scrubber still include several percent nitrous oxide. (See T. Suwa et al J. Chem. Soc. of Japan, *64* (11) 1879—1888, 1961). One of the big disadvantages of the conventional method therefore, is a large loss of nitrous oxide from the scrubber.

In accordance with the present invention, the gaseous product from the reactor after cooling, is first led into a purification ssytem

which comprises a scrubbing tower irrigated with alkaline solution, preferably operating at atmospheric pressure where higher nitrogen oxide by-products which are soluble in alkaline solutions may be removed.

The purified gas is then led into the concentration system which comprises systems for the absorption of gases by water under pressure and desorption systems used for releasing nitrous oxide by successive reduction of pressure. Two absorption vessels and two desorption vessels are used. Gases purified by the purification system are led to a first absorption tower in the concentration system in order to separate nitrogen and oxygen from nitrous oxide through absorption by water under superatmospheric pressure. The pressurized water containing nitrous oxide taken out from the bottom of the first absorption tower is led to a first desorption tower in order to release the concentrated nitrous oxide, which is in turn absorbed by water in a second absorption tower to undergo further concentration. Water that contains nitrous oxide is removed from the bottom of the second absorption tower and is led to a second desorption tower together with the water taken out from the bottom of the first desorption tower that still contains a considerable quantity of nitrous oxide in order to collect highly concentrated nitrous oxide by reducing the pressure. The nitrous oxide so recovered may then be dried and liquefied.

It is well known by those skilled in the art that where nitrogen oxides are produced from ammonia by catalytic oxidation the concentration of ammonia should be limited to below 10 percent to avoid any risk of explosion, due to the fact that an ammonia concentration of 15 per cent is the lower limit of explosion in both cases of ammonia-air and ammonia-oxygen mixture.

Obviously, in order to avoid any risk of explosion and maintain stabilized conditions for reaction, concentration of nitrous oxide should not exceed a few percent per pass for producing nitrous oxide by ammonia oxidation.

Using the process of the invention makes it possible to construct plant in compact shape, besides economizing the consumption of utilities and increasing the overall efficiency and the yield of nitrous oxide as compared with the conventional processes.

Figure 1 of the drawings shows a self-explanatory flow chart of one embodiment of the invention.

Figure 2 illustrates one embodiment of a multi-stage reactor suitable for use in the invention. It comprises a tower-type reactor (1) equipped with several layer-type beds carrying the catalyst (2) in which cooling systems (3) are inserted through which a heat exchange medium may be circulated. Six are shown.

It will be appreciated that it is not strictly necessary for the last catalyst bed to have a cooling system since the gaseous mixture formed therein is not being fed to a further catalyst bed but the presence of the cooling system will aid the cooling of the product gas mixture prior to purification.

At the start of the operation, the catalyst may be heated by said medium passing through the cooling system, and during the course of the operation, the heat generated by oxidation reaction will be removed by the same medium.

The invention is now illustrated by the following Example.

EXAMPLE

A mixture of 10.5% of ammonia, 89% of oxygen and 0.5% of nitrogen was fed at a rate of 100 liters per minute to the topmost layer of a multi-stage reactor equipped with six beds bearing bismuth-manganese oxide catalyst, while the temperature of the first layer of the catalyst was kept at 300—320°C. Ammonia was fed above each layer of the catalyst from the second to the sixth bed at a rate of 10 liters per minute and each of these second to sixth catalyst layers was kept at the temperature between 300 and 340°C, and the space velocity was kept within a range of between 1,000 and 1,500. After cooling the product gas mixture and purifying it to remove ammonia and other by-products such as nitrogen oxide and dioxide by scrubbing with aqueous alkali, a gaseous mixture containing 39.7% of nitrous oxide, 10.4% of nitrogen, and 49.9% of oxygen was obtained.

This gaseous mixture was compressed to a pressure of 20 kg/cm^2 (gauge) and fed continuously to the bottom of the first absorption tower where nitrous oxide was absorbed by water which was fed from the top of the tower counter-currently to the stream of gasas, and nitrogen and oxygen which are not absorbed by water were exhausted from the top of the absorption tower. Water containing nitrous oxide under pressure was led to the first desorption tower where 90% nitrous oxide was obtained by the reduction of pressure to 2 kg/cm^2 (gauge). The nitrous oxide of 90% purity was in turn absorbed by water in the second absorption tower. Water coming from both the first desorption tower and the second absorption tower was gathered and fed to the second desorption tower to reduce pressure to 0.1 kg/cm^2 (absolute), where nitrous oxide having an average concentration of 98.6% was produced. The total yield of nitrous oxide based on ammonia was 78.9%.

WHAT I CLAIM IS:—

1. A method of forming nitrous oxide by the catalytic oxidation of ammonia with oxygen, the method comprising causing a mixture of ammonia and oxygen to contact successively a plurality of spaced zones of catalyst arranged in series with the formation of nitrous oxide in each zone, cooling the gaseous mixture formed in each catalyst zone to a temperature not below the dew point of water in the mixture prior to feeding it to the next catalyst zone and causing it to contact the catalyst in the next zone together with added ammonia without separating the nitrous oxide, and recovering nitrous oxide from the product gas mixture obtained from the last zone.

2. A method as claimed in claim 1 in which at least three catalyst zones are used.

3. A method as claimed in claim 1 or claim 2 in which the cooling of the gas mixture is effected by means of indirect heat exchange with a heat abstraction medium circulating in the catalyst zone in which it is formed.

4. A method as claimed in any of claims 1 to 3 in which the catalyst zones are disposed one above the other in vertically spaced relationship in a tower reactor.

5. A method as claimed in any of claims 1 to 4 in which manganese-bismuth oxide is used as the catalyst.

6. A method as claimed in any of claims 1 to 5 in which the temperature of each catalyst zone is from 300 to 340°C.

7. A method as claimed in any of claims 1 to 6 in which the product gas mixture is cooled and the nitrous oxide is then recovered from it by

(i) scrubbing the product gas mixture with alkaline solution,

(ii) compressing the scrubbed product gas mixture,

(iii) feeding the compressed material to a first absorbing zone where it is exposed to water under pressure to absorb the nitrous oxide, and unabsorbed nitrogen and oxygen are removed,

(iv) exposing the water containing nitrous oxide to a lower pressure in a first desorption zone to release nitrous oxide,

(v) feeding the released nitrous oxide to a second absorbing zone where it is exposed to water under pressure and more unabsorbed nitrogen and oxygen are removed,

(vi) feeding water containing oxide from the first desorption zone and from the second absorbing zone to a second desorption zone where it is exposed to a lower pressure to release nitrous oxide, and

(vii) recovering the nitrous oxide.

8. A method as claimed in claim 7 in which the recovered nitrous oxide is dried and liquefied.

9. A method as claimed in claim 7 or claim 8 in which nitrogen and oxygen from step (iii) and/or step (v) are recirculated for inclusion in the reaction mixture of ammonia and oxygen.

10. A method for the production of nitrous oxide by the catalytic oxidation of ammonia by oxygen in a plurality of catalyst zones, substantially as hereinbefore described.

11. A method for the production of nitrous oxide by the catalytic oxidation of ammonia by oxygen in a plurality of catalyst zones, substantially as shown in the Example.

12. Apparatus for the production of nitrous oxide by the catalytic oxidation of ammonia by oxygen comprising a multi-stage reactor having means for supporting at least two catalyst beds in series, the catalyst beds being spaced from one another, means for supplying a reaction mixture of ammonia and oxygen to the first catalyst bed, means for supplying a reaction mixture comprising fresh ammonia and the gaseous product of the previous catalyst bed to each succeeding catalyst bed after the first, and means associated with at least each of the catalyst beds except the last for circulating a heat-abstraction medium within the catalyst bed for indirect heat exchange with the gaseous reaction mixture in that bed.

13. Apparatus as claimed in claim 12 in which the catalyst beds are arranged to be disposed one above the other in vertically spaced relationship in a tower reactor.

14. Apparatus as claimed in claim 12 or claim 13 which comprises additionally:

(i) a purification vessel for the nitrous oxide containing product gas mixture from the multi-stage reactor comprising a gas inlet and gas outlet and an inlet and outlet for alkaline solution,

(ii) a compressor connected to the gas outlet of the purification vessel for compressing the purified gas mixture from the purification vessel,

(iii) a first absorption vessel with a water inlet, a gas inlet connected to the outlet from the compressor, a gas outlet for unabsorbed gases comprising nitrogen and oxygen and a separate outlet for the water containing absorbed nitrous oxide.

(iv) a first desorption vessel having an inlet connected to the water outlet of the first absorption vessel, said desorption vessel having a gas outlet for the desorbed nitrous oxide and a liquid outlet for the water,

(v) a second absorption vessel with a water inlet, a gas inlet connected to the gas outlet for nitrous oxide from the first desorption vessel, and separate outlets for the water containing absorbed nitrous oxide and the unabsorbed gas comprising nitrogen and oxygen, and

(vi) a second desorption vessel supplied by the water outlets of the first desorption vessel and the second absorption vessel, and having an outlet for the nitrous oxide desorbed from the water and an outlet for the water.

15. Apparatus as claimed in claim 14 in which means are provided for supplying the unabsorbed gases comprising nitrogen and oxygen from the first and second absorption vessels to the inlet to the multi-stage reactor.

16. Apparatus as claimed in any of claims 12 to 15 which additionally comprises means for drying the nitrous oxide obtained from the second desorption vessel and means for liquefying the dried nitrous oxide.

17. Apparatus for the production of nitrous oxide, substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawings.

18. Nitrous oxide obtained by the method claimed in any of claims 1 to 11.

19. Nitrous oxide obtained by using the apparatus claimed in any of claims 12 to 17.

MATHYS & SQUIRE,
Chartered Patent Agents,
10 Fleet Street,
London, E.C.4.
Agents for the Applicant.

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FIG. 1.

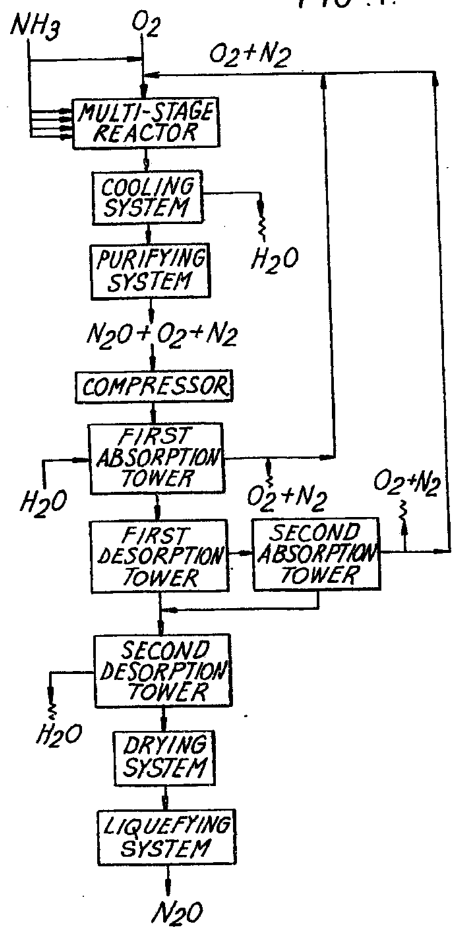

FIG. 2.